*Indian J. Phys.* **72A** (2), 99–105 (1998)

**IJP A**
— an international journal

# Optical and structural characterisation of ZnO films prepared by the oxidation of Zn films

Benny Joseph, K G Gopchandran, P K Manoj, J T Abraham, Peter Koshy* and V K Vaidyan

Department of Physics, University of Kerala, Kariavattom, Trivandrum-695 581, India

*Regional Research Laboratory, Pappanamcode, Trivandrum-695 019, India

*Received 4 September 1997, accepted 13 January 1998*

**Abstract** : Zinc oxide films have been prepared by the post-deposition heat treatment of zinc films. X-ray diffraction studies have confirmed the preferential orientation of the films along (002) plane. The texture coefficient has been calculated to explain the preferential orientation. SEM studies have revealed a faceted elongated microstructure. From the transmission spectra optical bandgap has been determined as 3.3 eV.

**Keywords** : Zinc oxide, annealing, bandgap

**PACS Nos.** : 81.15Gh, 81.40Gh

## 1. Introduction

ZnO is a multifunctional material with a wide area of applications. ZnO films have attracted considerable attention because they can be made to have high electrical conductivity, high infrared reflectance and high visible transmittance. The constituent elements of the film are abundantly available at low cost and are nontoxic. Aktaruzzaman *et al* [1] and Minami *et al* [2] have reported that ZnO films are known to be more resistant to the reduction by hydrogen containing plasma than the conventional transparent conductors tin oxide and indium oxide. Zinc oxide is an *n*-type semiconductor with hexagonal wurtzite structure and a bandgap of 3.3 eV [3]. Pure zinc oxide is transparent in the visible region and it has low conductivity and low infrared reflectance. The nonstoichiometric zinc oxide films are the simplest, most economical to prepare and their electrical and optical properties are also excellent.

Zinc oxide films have potential applications in energy efficient windows, solar cells, liquid crystal displays, optoelectronic devices, gas sensors, piezoelectric devices, *etc.* Zinc oxide films have been deposited by different methods such as evaporation [4], spray pyrolysis [5], chemical vapour deposition [6], magnetron sputtering [7] and laser ablation technique [8]. Only few reports are available on the formation of zinc oxide films by evaporation technique. In this paper, we report the deposition of zinc oxide films on glass substrates by post-deposition heat treatment of zinc films. The structural properties of the films and their morphological and optical properties are investigated.

## 2. Experimental

Thin films of zinc were prepared on glass substrates at room temperature by resistive heating of metallic zinc under a vacuum of ~$10^{-5}$ mbar. It is necessary to use a zinc source that is almost enclosed since the emission rate has to be controlled [9]. These films were subjected to post-deposition heat treatment above the melting point of zinc (693 K). As-deposited films annealed at 723, 773, 823 and 873 K for 30 min were cooled slowly at a rate of 9 K/min to room temperature. The X-ray diffraction studies were conducted on a Philips PW 1701 powder crystallography instrument using $CuK_\alpha$ radiation. The surface morphology of the films were evaluated by using JEOL 35C scanning electron microscope. The optical transmission studies were performed using a Shimadzu double beam spectrophotometer UV 240 in the range 300–900 nm.

## 3. Results and discussion

The X-ray diffraction peaks of the films are readily indentifiable and their position concide with reflections reported in the ASTM diffraction pattern file for powder ZnO [10]. Figure 1 depicits the X-ray diffraction patterns for films annealed at various temperatures. The presence of many peaks indicate the polycrystalline structure of the films. The strongest diffraction peak at all annealing temperatures is along (002) crystal plane with $2\theta = 34.4°$. This pronounced peak indicate that the preferred orientation of the microcrystals of the film is along the *c*-axis normal to the substrate surface. The preferred orientation of the microcrystals was found in the case of films prepared using other methods [11,12]. The other peaks observed with less intensity are (100) and (101) with $2\theta$ values about 31.7 and 36.3 degree respectively. The XRD data of the film annealed at 723 K reveals that the films contain slight amount of metallic zinc. This indicates that the oxidation is incomplete at 723 K. In all the other diffractograms the phases identified are those of zinc oxide. Each grain in a polycrystalline film normally has a crystallographic orientation different from that of its neighbours. Considered as a whole, the orientations of all grains may be randomly distributed in relation to some selected frame of reference or they may tend to cluster, to a greater or lesser degree, about a particular orientation or a few orientations. Any polycrystalline material characterised by the above condition is said to have a preferred orientation or texture. When cold worked material pocessed of deformation texture is crystallised by annealing, the new grain structure usually has a preferred orientation different from that of cold worked

material. This is called annealing texture [13]. In the present investigation the films exhibited a preferred orientation along (002) diffraction plane. To describe this orientation,

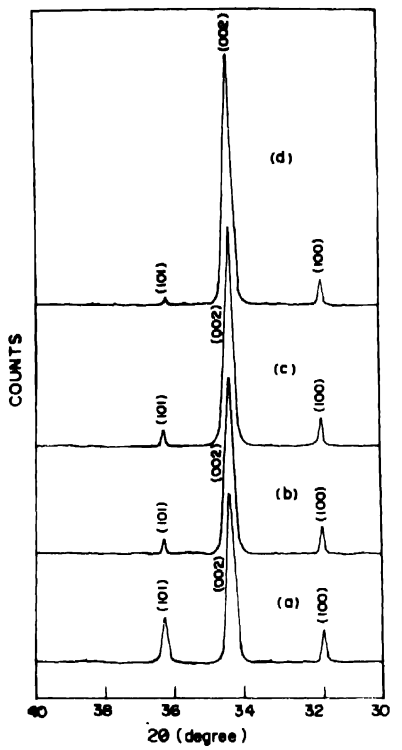


**Figure 1.** X-ray diffractograms of zinc films prepared at different annealing temperatures : (a) 723, (b) 773, (c) 823 and (d) 873 K

texture coefficient TC (*hkl*) is calculated for planes (002), (100) and (101) using the expression [14]

$$\mathrm{TC}(hkl) = \frac{I(hkl)/I_0(hkl)}{\frac{1}{N}\sum I(hkl)/I_0(hkl)}, \tag{1}$$

where $I$ is the measured intensity, $I_0$ is the ASTM standard intensity of the corresponding powder sample and $N$ the reflection numbers. From the defenition, it is clear that the deviation of the texture coefficient from unity implies the preferred orientation of the growth. Figure 2 shows the variation of texture coefficient with annealing temperature for diffraction peaks along the planes (002), (100) and (101). The texture coefficient along the (002) crystal plane (TC (002)) increases with substrate temperature and is found to be maximum for films annealed at 873 K. The preferred orientation along (002) is associated with the increased number of crystallites along that plane. The values of TC (100) and TC

(101) are gradually decreasing with increase of annealing temperature. A marked seperation of the high angle in the X-ray diffraction peaks of the $K\alpha_1$ and $K\alpha_2$ line is also observed. The crystallite size $D$ along $c$-axis can be estimated by [13] :

$$D = \frac{0.9\,\lambda}{B\cos\theta}, \tag{2}$$

where $\lambda$ is the X-ray wavelength, $\theta$, the Bragg diffraction angle and $B$, the full width at half maximum (FWHM) for the films prepared. The lattice parameters are calculated from the

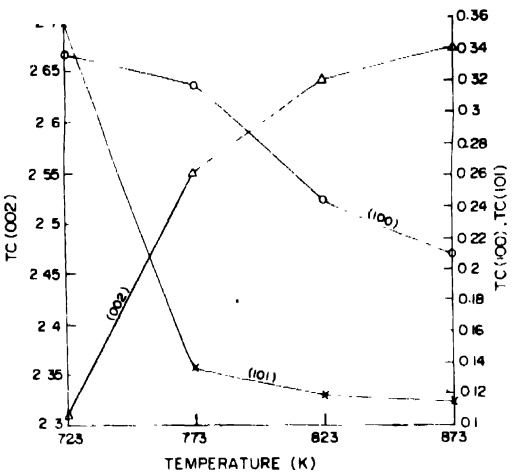


**Figure 2.** Variation of texture coefficients TC (002), TC (100) and TC (101) as a function of annealing temperature

X-ray diffractogram of the films and the values obtained are consistent with the values given in the ASTM data and are listed in Table 1.

**Table 1.** Microstructural parameters associated with ZnO films.

| Annealing temperature (K) | Grains size (nm) | Lattice parameters (nm) | |
|---|---|---|---|
| | | $a_0$ | $c_0$ |
| 723 | 50 | 0.3254 | 0.5210 |
| 773 | 66 | 0.3253 | 0.5206 |
| 823 | 36 | 0.3255 | 0.5208 |
| 873 | 66 | 0.3262 | 0.5212 |
| ASTM | | 0.3249 | 0.5205 |

The strongly textured thin films, presenting intense diffraction peaks with small width at half maximum, have high resistivities [15]. Our measurements quantitatively support this fact and the samples were of high electrical resistivity.

***Plate I***

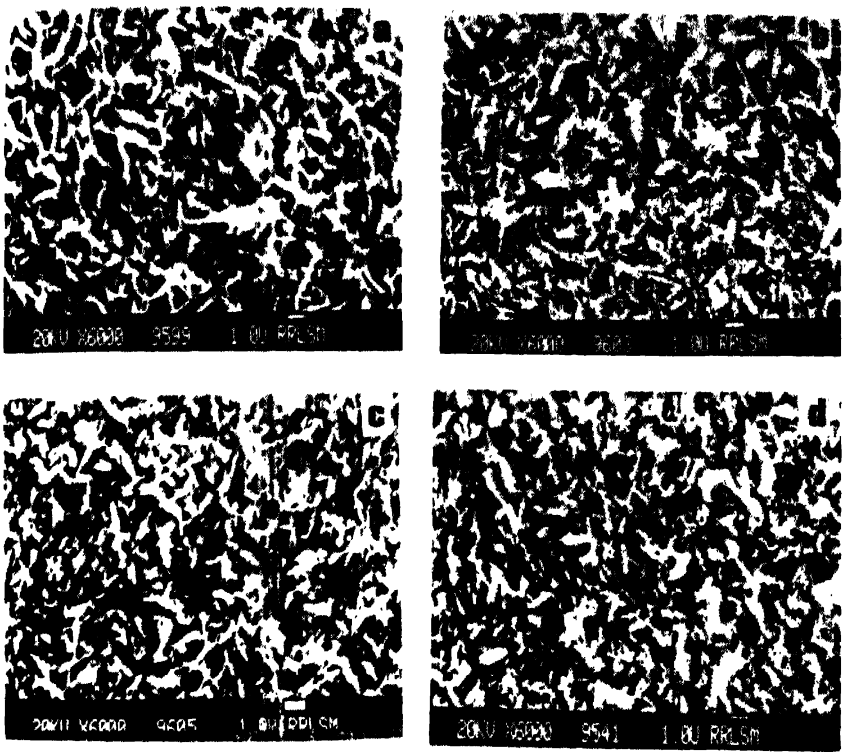


**Figure 3.** Scanning electron micrographs of zinc films annealed at different temperatures : (a) 723, (b) 773, (c) 823 and (d) 873 K.

The scanning electron micrograph of these films were taken to evaluate their surface morphology. Figure 3 depicits the scanning electron micrograph of the films annealed at 723 [Figure 3(a)], 773 [Figure 3(b)], 823 [Figure 3(c)] and 873 K [Figure 3(d)]. The structural studies have revealed the strong intensity of the (002) peak, indicating that the grains have *c*-axis perpendicular to the substrate surface. The micrographs indicate a textured morphology with network like structures at all annealing temperatures similar to other investigators [16,17]. The surface morphology reveals a faceted elongated microstructure. The network like structure seen on the micrograph deteriorate with increase of annealing temperature.

The optical transmission spectra of the films were studied in the wavelength region 300–900 nm. The intrinsic absorption in a semiconductor occurs for wavelengths in the vicinity of the energy gap. The transmission spectrum of the film of thickness ~150 nm annealed at 873 K is shown in Figure 4. The absorption coefficient $\alpha$ was calculated following the Lamberst's law and was calculated as :

$$\alpha = \frac{2.303 \times A}{t}, \tag{3}$$

where $A$ is the optical density which was taken directly from the transmission spectrum and $t$, the film thickness. Figure 5 depicits the typical variation of absorption coefficient $\alpha$ with photon energy. The absorption has its minimum value at its low energy and increases

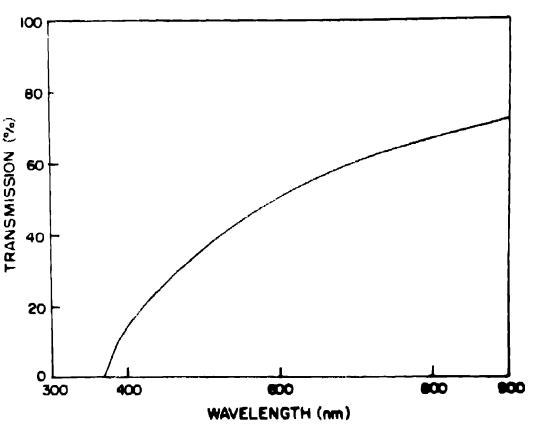


**Figure 4.** Transmission spectrum of zinc oxide films prepared by the post-deposition annealing of zinc films at 873 K.

with optical energy in a similar manner to the absorption edge of the semiconductor. It can be seen that this film shows a high absorption ($\alpha \sim 10^4$ cm$^{-1}$). The increase of transmittance with wavelength in the transmission spectrum (Figure 4) may be due to the existence of large number of levels in the forbidden gap just below the conduction or just

above the valence band. Because of the large absorption before the absorption edge, interference fringes are absent and consequently the refractive index of the film could not be determined.

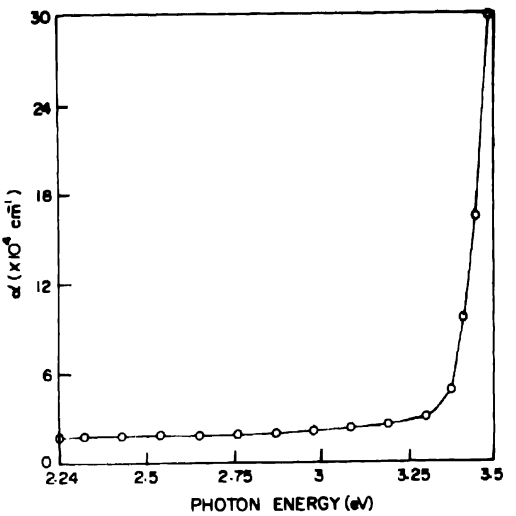


**Figure 5.** Absorption coefficient ($\alpha$) *versus* photon energy ($h\nu$) of zinc oxide films prepared by the post-deposition annealing of zinc films at 873 K.

Assuming that the transition probability becomes constant near the absorption edge, the absorption coefficient $\alpha$ for directly allowed transition for simple parabolic band scheme can be described as a function of incident photon energy $h\nu$, as [18] :

$$\alpha \propto (h\nu - E_g)^{1/2}, \tag{4}$$

where $E_g$ is the optical bandgap. The extrapolation of the linear portion of the graph $\alpha^2$ *vs* $h\nu$ to the $h\nu$ axis gives the value of the band gap and is found to be 3.3 eV for the sample annealed at 873 K in good agreement with the reported values [19,20].

## 4. Conclusion

Polycrystalline zinc oxide thin films are prepared by the post-deposition annealing of evaporated zinc films in the range 723–873 K. The grains of the films have preferred orientation along (002) plane and the texture coefficient increases with annealing temperature. The lattice parameters calculated are consistent with the ASTM data. Surface morphology analysis has revealed a faceted elongated microstructure. The optical absorption shows that the fundamental absorption starts at 3.3 eV and the transition leading to this is a directly allowed one.

**References**


[1] A F Aktaruzzaman, G L Sharma and L K Malhotra *Thin Solid Films* **198** 67 (1991)

[2] T Minami, H Nanto and S Takata *Appl. Phys. Lett.* **41** 58 (1982)

[3] J Hu and R G Gordon *J. Electrochem. Soc.* **139** 2014 (1992)

[4] H Watnabe *Jpn. J. Appl. Phys.* **9** 418 (1970)

[5] J Arnovich, A Ortiz and R H Bube *J. Vac. Sci. Technol.* **16** 994 (1979)

[6] A P Roth and D F Williams *J. Appl. Phys.* **52** 4260 (1981)

[7] Y Igasaki and H Saito *J. Appl. Phys* **69** 2190 (1991)

[8] H Sankur and J T Cheung *J. Vac. Sci. Technol* **A1** 1806 (1983)

[9] L Holland *Vacuum Deposition of Thin Films* (London · Chapman & Hall) p 180 (1970)

[10] Powder Diffraction File Data card no. 5-664 JCPDS (Internationl Centre for Diffraction data, Swartmore, PA)

[11] D Cossement and J M Streydio *J Cryst Growth* **72** 57 (1985)

[12] Y E Lee, J B Lee, Y J Kim, H K Yang, J C Park and Y J Kim *J. Vac. Sci Techol.* **A14** 1943 (1996)

[13] B D Cullity *Elements of X-ray Diffraction* (Reading, MA : Addison Wesley) p 284, 295 (1956)

[14] C Barret and T B Massalski *Structure of Metals* (Oxford : Pergamon) p 204 (1980)

[15] Li-jian Meng, M Andritschky and M P Dos Santos *Vaccum* **44** 109 (1993)

[16] Yoshino, W W Weans, A Yamada, M Konagai and K Takahashi *Jpn. J. Appl Phys* **32** 726 (1993)

[17] W W Weans, M Yoshino, K Tabuchi, A Yamada, M Konagai and K Takahashi *Proceedings of 22nd IEEE PVSC* 935 (1993)

[18] A Abeles *Optical Properties of Solids* (Amsterdam . North Holland) p 32 (1992)

[19] A P Roth and D F Williams *J Appl. Phys.* **52** 6686 (1981)

[20] Chris Ebrspacher, A L Fahrenbruch and R Bube *Thin Solid Films* **136** 1 (1986)